



Short communication

An advanced configuration $\text{TiO}_2/\text{LiFePO}_4$ polymer lithium ion batteryJusef Hassoun^{a,*}, Manuel Pfanztel^b, Pierre Kubiak^b, Margret Wohlfahrt-Mehrens^b, Bruno Scrosati^a^a Department of Chemistry, University of Rome “La Sapienza”, 00185 Rome, Lazio, Italy^b Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Helmholtzstr 8, 89081 Ulm, Germany

HIGHLIGHTS

- ▶ A lithium ion battery with TiO_2 anode and LiFePO_4 cathode is here reported.
- ▶ The battery operates with 1.8 V voltage and 150 mA h g^{-1} specific capacity.
- ▶ The system has a solid polymer configuration.
- ▶ The battery has high safety level and remarkable environmental compatibility.

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ABSTRACT

In this paper we report a solid state lithium ion battery based on nanostructured titanium oxide (TiO_2) anode, olivine lithium iron phosphate (LiFePO_4) cathode and polyethylene oxide (PEO)-based electrolyte. The battery evidences average working voltage of 1.8 V and specific capacity of 150 mA h g^{-1} . The solid cell configuration is characterized by enhanced electrochemical properties, high safety level and remarkable environmental compatibility. The preliminary results here reported suggest that the system may be suitable to be used as alternative energy storage system for powering safe and environmental friendly hybrid and electric vehicles.

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1. Introduction

Lithium ion batteries are very appealing energy storage systems characterized by very high energy and power density in comparison with conventional batteries [1,2]. Modern lithium ion accumulation systems are considered very promising power tools for electric or hybrid vehicles with performance comparable to that of oil-fuelled cars [3]. Furthermore, the replacement of combustion engine with electric may strongly contribute to the control of the global warming and the air quality in urban areas. Particular attention is presently devoted to the increase of the safety level of the battery in order to make it really suitable to be used in the electric vehicles. This important goal can be reached by modifying the cell configuration, i.e. by changing the electrode and the electrolyte components. The present configuration lithium ion battery involves a graphite anode, a lithium cobalt oxide cathode, and a liquid organic-solution electrolyte. Cobalt is toxic and expensive

metal and graphite is characterized by a very low working voltage, i.e. 0.2–0.01 V vs. Li, which is out of the electrochemical stability windows of the organic electrolyte that is, in addition, toxic and flammable [4]. These issues negatively influence the cost and the safety level of the battery.

Recently, several combinations of electrodes have been reported in literature, including layered structure, olivine, and spinel-structure cathodes, graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li-alloying anodes and gel-polymer or plasticized polymer electrolyte [5,6]. Among the cathodes the lithium iron phosphate has revealed to be very promising material, characterized by a two-phase electrochemical process with stable working voltage of 3.5 V vs. Li and specific capacity of 170 mA h g^{-1} [7–9]. Furthermore, the titanium oxide anode in its various polymorphs, i.e. anatase, brookite and rutile, characterized by reversible insertion at 1.4–1.8 V vs Li and capacity ranging between 170 and 330 mA h g^{-1} , attracted large attention [10–13]. LiFePO_4 and TiO_2 electrodes, operating in the stability window of common liquid electrolytes, are in addition characterized by low cost and high environmental compatibility. New, safe and easily scalable electrolytes are even more attracting than

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the electrode materials. Very interesting examples are the poly(ethylene oxide)-based, PEO–LiX, electrolytes, i.e. amorphous solid membranes in which the PEO chains assure the lithium ion transport, the chemical and the mechanical stability [14,15]. Generally, dispersion of nanosize-ceramic fillers, such as ZrO_2 , Al_2O_3 , SiO_2 , into the PEO-based polymer matrix, is used in order to increase the ionic conductivity and mechanical stability [16–18].

LiFePO_4 cathode, PEO-based electrolyte and TiO_2 anode are well known materials however their combination in a lithium ion cell has never been reported since it requires a full understanding of the electrode–electrolyte interface, including the electrolyte decomposition processes effect on the cell balance and on its electrochemical performances. TiO_2 is a very safe and environmentally friendly electrode, however it is characterized by surface reactivity with the electrolytes, with consequent formation of SEI film and associated irreversible capacity during the first cycle, as commonly observed for the Li-ion anode materials [19]. This issue, strongly depending on crystallite size and material morphology [20], is particularly affective for the nanostructured TiO_2 that has the advantage of a higher reversible capacity in respect to the conventional material [21]. A polymer cell using TiO_2 anode, LiFePO_4 cathode and PEO-electrolyte is supposed to have high safety level mainly due the following reasons:

- i) The cell completely avoids the common flammable organic electrolytes, characterized by a remarkable difference between heat generation and heat dissipation leading to exothermal reaction with self-sustained increase in cell heating (thermal run-away) [22] and possible dramatic failure with violent venting and explosion of the cell [23];
- ii) The cell is lithium metal-free, with no hazard associated with the extreme reactivity by accidental contact with the ambient moisture. Certainly, these important safety features should be confirmed by specific, industrial-type, tests performed on a real cell prototypes.

Further appealing properties of the solid-polymer lithium ion cell are the very low toxicity and the low cost of the employed materials, i.e. LiFePO_4 , TiO_2 and PEO, in comparison with those in the present-technology cells containing toxic and expensive metals and solvents, such as Co, EC, DMC.

In this paper we exploited the above described TiO_2 /PEO-electrolyte/ LiFePO_4 lithium ion cell. Prior to polymer cell study, a preliminary, routine-characterization of the LiFePO_4 and of the nanostructured TiO_2 electrodes in conventional liquid electrolyte has been performed, this with the aim to optimize the final cell set-up and its operating condition. Furthermore, we have performed a proper surface activation of the nanostructured TiO_2 electrode capable to address the first cycle irreversible capacity drawback, and an impedance spectroscopy study evidencing that the electrolyte reaches ionic conductivity suitable for lithium cell applications at temperatures exceeding 60 °C. The results demonstrated that the cell is characterized by a working voltage of 1.8 V and a capacity of 150 mA h g^{-1} .

2. Experimental

2.1. The materials

Carbon-coated LiFePO_4 has been synthesized by combining wet-chemistry and calcination processes as described in a previous work [24].

The synthesis of the nano-sized TiO_2 , already reported in previous papers [21,25], basically involved the dissolution of sodium dodecyl sulphate in dilute hydrochloric acid, followed by

the addition of a bis 1,2,3 trihydroxypropyl titanate, ultrasonication at 60 °C for 2 h, ageing overnight, washing of the powder and final calcination at 400 °C for 4 h.

The $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3 + 10\%$ w:w ZrO_2 electrolyte was prepared following the procedure described in detail in a previous paper [17]. The electrolyte components, PEO 6 · 10⁵ mw, LiCF_3SO_3 salt and ZrO_2 ceramic powder (Aldrich) were carefully dried, sieved and then introduced in their correct proportion inside sealed polyethylene bottles. The bottles were thoroughly mixed by soft glass ball-milling for at least 24 h to obtain a homogeneous mixture of powders. To avoid any contamination with external ambient, all the samples were prepared in a controlled, argon atmosphere, dry box. Homogeneous, rigid membrane samples, having thickness ranging from 100 μm to 300 μm , were obtained after hot pressing at 90 °C and 4 tons for 1 h.

X-ray diffraction (XRD) measurements were performed using a Siemens D5000 with Cu K α radiation ($\lambda = 0.154$ nm). Scanning electron microscopy (SEM) images were collected on a Leo 1530 VP. Transmission electron microscopy (TEM) was carried out by a Titan 80–300 kV.

2.2. The electrochemical characterisation

TiO_2 electrodes with a loading of 2 mg cm^{-2} have been manufactured by preparing a slurry with 76:12:12 wt% composition of active material, Super P carbon and polyvinylidene fluoride (PVDF), respectively. Same method is used to prepare LiFePO_4 electrode with a composition of 80:10:10 wt%. The TiO_2 and LiFePO_4 slurries were coated on a copper and an aluminium foil, respectively, as the current collector using the “doctor blade” technique with a thickness of 150 μm and then dried at 40 °C 1 h⁻¹. Circular electrodes were punched from the foils, pressed, and then dried at 130 °C under vacuum overnight. The electrochemical measurements of the half cells were performed with three-electrode cells assembled in an argon glove box MBRAUN. Metallic lithium was used as counter and reference electrodes, a glass microfiber (Whatman GF/A), as a separator, and 1 M LiPF_6 in ethylene carbonate:dimethyl carbonate, EC:DMC, 1:1 wt%, solution (UBE Industry, Japan) as electrolyte. The maximum x in Li_xTiO_2 was assumed to be 1 (corresponding to 335 mA h g^{-1}), and thus, the charging rates in these measurements were based on a 1C rate of 0.335 A g^{-1} . For the LiFePO_4 electrode 1C rate current was considered as 0.17 A g^{-1} .

The full cells were assembled by coupling the TiO_2 anode and the LiFePO_4 cathode using a standard EC: DMC, 1:1, LiPF_6 1 M liquid electrolyte and a $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$ –10% ZrO_2 polymer electrolyte membrane. Half cells and liquid electrolyte-full cell measurements were carried out at room temperature using a VMP/Z (Princeton, Biologic) electrochemical workstation, while polymer electrolyte-full cell has been cycled at 90 °C using a Maccor Series testing system. Prior to liquid electrolyte-full cell testing, the LiFePO_4 cathode was de-lithiated by charging it against the third metallic lithium electrode from the open circuit voltage (OCV) up to 4 V at C/5 rate (1C = 0.170 A g^{-1}) while the TiO_2 anode was lithiated by charging it against the third lithium electrode from OCV to 1 V at C/5 rate (1C = 0.335 A g^{-1}). Finally, the full cell in the charged state was discharged up to 0.8 V at C/5 rate (1C rate was referred to the LiFePO_4 active mass as 0.17 mA g^{-1}). After the above described activation procedure, the full cell was cycled at C/3 rate within 0.8–3.8 V limits. This procedure is hereafter indicated as electrochemical, indirect, activation [26]. For solid electrolyte-full cell application, the TiO_2 electrode has been surface-treated under argon atmosphere by placing it in direct contact with lithium metal foil wet by the EC-DMC, 1:1, LiPF_6 electrolyte for 5 min, at a pressure of 0.4 kg cm^{-2} . Subsequently, the lithium foil and the excess of electrolyte were removed, and the lithium free full cell was

assembled coupling the surface-treated TiO_2 electrode and the LiFePO_4 electrode in the PEO-electrolyte, aged at 90°C for 12 h, and cycled at $C/3$ rate within 0.5–3.5 V limits. This procedure is therefore indicated as direct activation [6].

The ionic conductivity measurements of the solid polymer electrolyte were carried out by AC impedance spectroscopy, using a VersaStat Ametek instrument with cells prepared by housing electrolyte membrane samples having an 8-mm diameter and 100 μm of thickness in a Teflon O-ring and sandwiching them between two blocking stainless steel electrodes. The cells were heated to about 120°C and kept at this temperature for 24 h to reach the thermal equilibrium. The measurements were performed in the 120 – 40°C temperature range at both cooling and heating scans.

3. Results and discussion

The structure and the morphology of the TiO_2 and LiFePO_4 electrodes are detected by XRD, SEM and TEM, respectively. The XRD patterns of Fig. 1A reveal the formation of crystalline rutile (JCSd #77-0443) and the data refinement indicates a crystallite diameter lower than 10 nm. A sub-micrometric, sphere-like morphology with randomly dispersed rods is clearly observed by the SEM image of Fig. 1B, while nano-size, whiskerlike-shape, crystals are evidenced by the TEM of Fig. 1C, as also observed by previous studies [21,25]. The LiFePO_4 powder is characterized by a well defined crystalline structure (JCSd #83-2092, see XRD patterns of Fig. 1D) and a crystallite size of about 98 nm, with micrometric morphology, see SEM images of Fig. 1E.

Half lithium cells using the two electrodes in a standard EC:DMC, 1:1, LiPF_6 1 M electrolyte have been assembled and galvanostatically cycled in order to find the electrochemical setup suitable for the new lithium ion cell. Then, the electrodes have been

coupled in a lithium ion cell using the same electrolyte. Fig. 2 reports the galvanostatic voltage profiles of the lithium cells using the TiO_2 and the LiFePO_4 electrodes (A) and of the $\text{LiFePO}_4/\text{TiO}_2$ lithium ion cell (B). The Fig. 2A shows an average working voltage of about 3.5 V vs. Li for the LiFePO_4 electrode and of about 1.7 V vs. Li for the TiO_2 electrode half cell, with specific capacities of the order of 150 and 200 mA h g^{-1} , respectively. The half-cell current rates, i.e. $C/3$ for LiFePO_4 and $C/5$ for the TiO_2 electrode, have been selected taking into account the differences between the theoretical specific capacities of the two materials leading to different 1C current value (0.170 and 0.335 A g^{-1} , respectively), this in view of full cell application. Furthermore, the Fig. 2A evidences a first cycle irreversible capacity of the order of 20% and of 25% of the initial capacity, i.e. 34 and 75 mA h g^{-1} , for the LiFePO_4 and the TiO_2 electrode, respectively, most likely associated with the decomposition of the electrolyte on the electrode surface with formation of solid electrolyte interface (SEI) and with the electrode-structure reorganization [19,21,27]. Prior to full cell testing, the issue of the initial irreversible capacity, that may negatively affect the cell behaviour, has been addressed by electrochemical activation of the electrodes, see Experimental part, so that the resulting lithium ion battery evidenced enhanced electrochemical behaviour at $C/3$ rate with stable capacity of the order of 150 mA h g^{-1} (see inset of Fig. 2B) and voltage signature evolving at about 1.8 V (see Fig. 2B) reflecting the process $\text{TiO}_2 + x\text{LiFePO}_4 = \text{Li}_x\text{TiO}_2 + x\text{FePO}_4$.

A full cell with the same electrodes configuration has been assembled using a solid electrolyte with composition of $\text{PEO}_{20}\text{-LiCF}_3\text{SO}_3 + 10\%$ w:w ZrO_2 . This electrolyte has been previously investigated by meaning of impedance spectroscopy to follow its conductivity at the various temperatures. Fig. 3, reporting the Arrhenius plot of the electrolyte, evidences that temperatures higher than 60°C promote conductivity values suitable for battery application, i.e., higher than $10^{-4} \text{ S cm}^{-1}$.

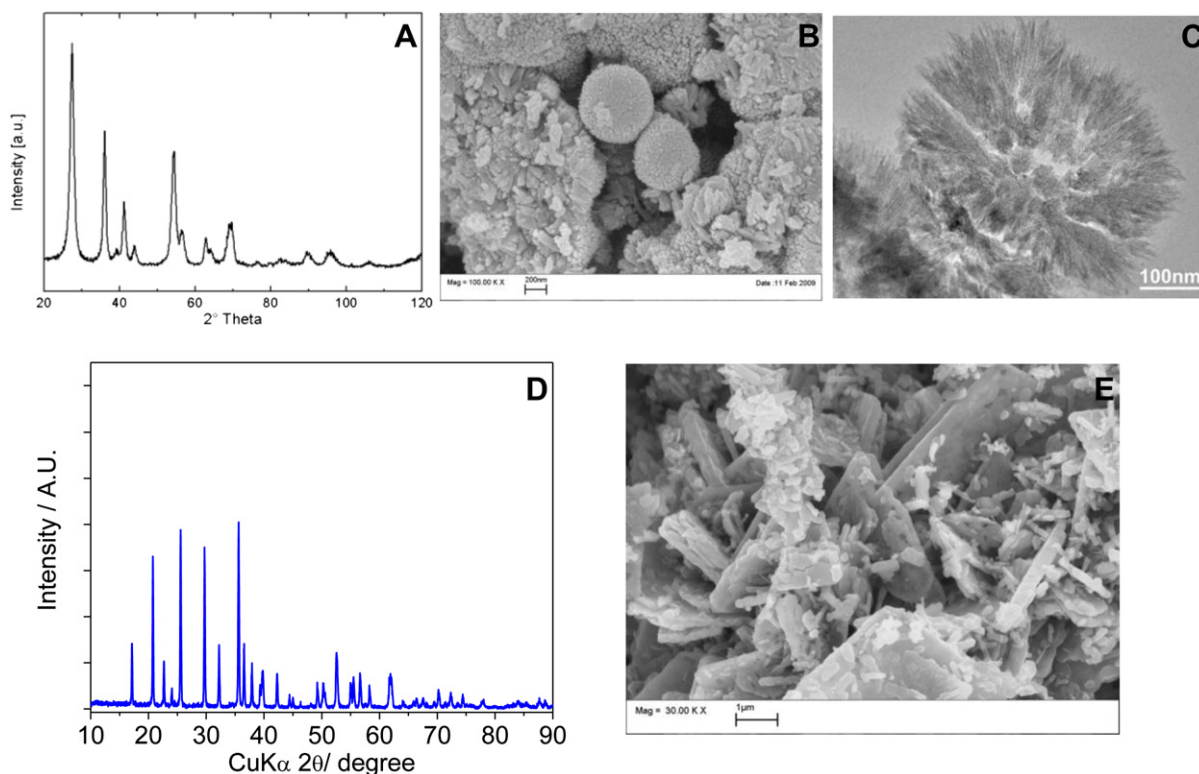


Fig. 1. (A) X ray diffraction patterns (XRD), (B) Scanning electron microscopy (SEM) and (C) transmission electron micrographs (TEM) of the TiO_2 electrode. (D) X ray diffraction patterns (XRD) and (E) Scanning electron microscopy (SEM) of the LiFePO_4 electrode.

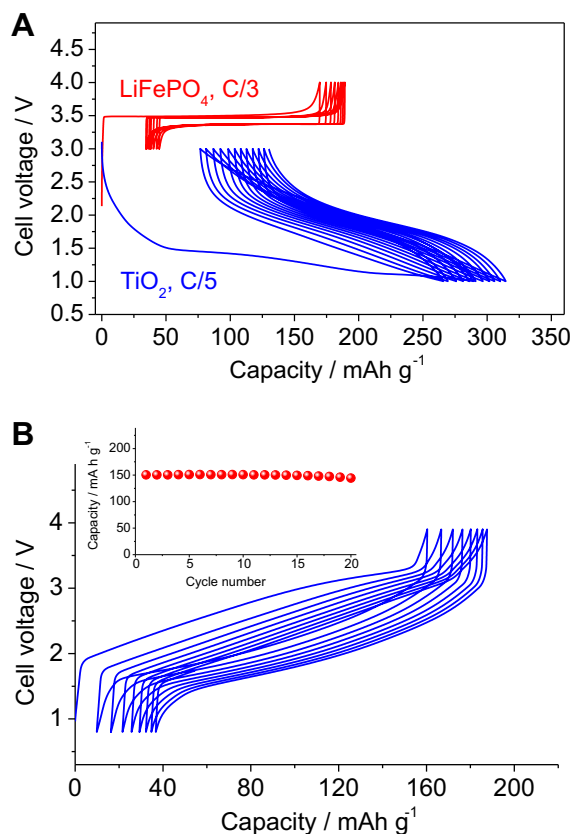


Fig. 2. A) Voltage profile of the galvanostatic tests performed on lithium cells using the TiO₂ electrode at C/5 rate ($1C = 0.335 \text{ A g}^{-1}$) in the 1–3 V vs. Li voltage range and the LiFePO₄ electrode at C/3 rate ($1C = 0.170 \text{ A g}^{-1}$) in the 3–4 V vs. Li voltage range. B) Voltage profile and in inset cycling behaviour of the galvanostatic test performed on the LiFePO₄/TiO₂ lithium ion cell performed at C/3 rate ($1C = 170 \text{ mA g}^{-1}$) in the 0.8–3.8 V voltage range. EC:DMC 1:1, LiPF₆ 1 M electrolyte. Room T.

In view of the full-solid cell application, the TiO₂ electrode has been surface-treated with lithium metal, see [Experimental](#) part, to reduce the irreversible capacity of the first cycle, this in alternative to the “indirect” electrochemical activation above adopted for the liquid electrolyte full cell. The direct activation procedure, originally employed for the tin-carbon nanostructured electrode

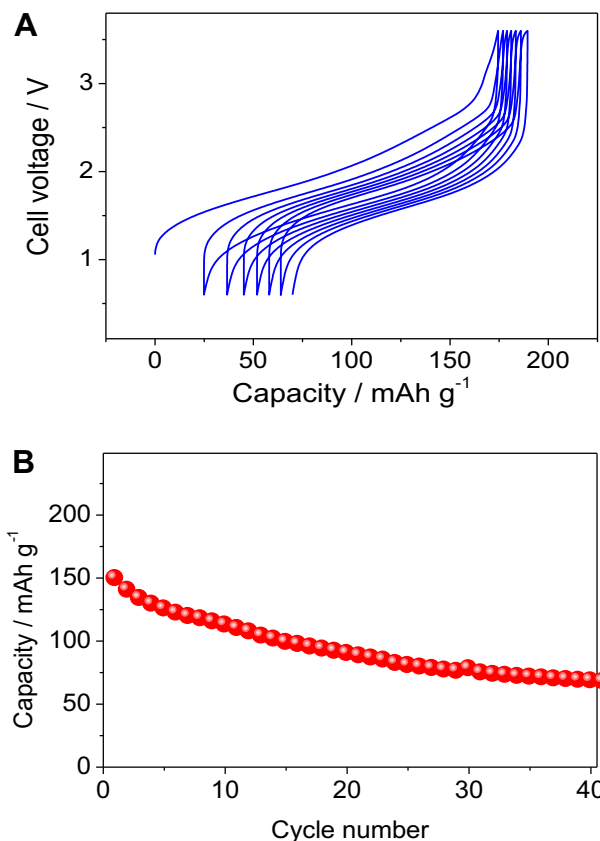


Fig. 4. Voltage profile (A) and cycling behaviour (B) of the galvanostatic test performed at 90 °C and at C/3 rate of the LiFePO₄/TiO₂ lithium cell. PEO₂₀LiCF₃SO₃ + 10% w:w ZrO₂ solid electrolyte. Voltage limits 0.5–3.5 V vs. Li, 1C rate 0.170 A g⁻¹.

[6,28], consisted in a chemical reduction of the electrode by using a lithium metal foil wetted by EC:DMC-LiPF₆ electrolyte. After removing the lithium foil and the electrolyte excess, this operation allowed to pre-form a SEI film on the electrode surface. The direct activation, having the advantage of being easily up scalable to industrial roll-to-roll systems, is of crucial importance since it produces electrodes with very low irreversible capacity during operation, with associated positive effects on the full cells balance. After direct activation of the TiO₂ electrode, the full cell has been assembled coupling it with the LiFePO₄ electrode in the solid PEO membrane. The cell was conditioned at 90 °C to reach the proper conductivity level and cycled at a C/3 rate at the same temperature. The [Fig. 4](#), reporting the voltage profile (A) and cycling behaviour (B) of the cell, evidences the reproducibility during the initial cycles of the expected voltage signatures with an average voltage of 1.8 V, and with an initial specific capacity of the order of 150 mA h g⁻¹ versus the LiFePO₄ electrode mass (see [Fig. 4A](#)).

However, a decay of the capacity is observed in the following cycling with stabilization at 75 mA h g⁻¹ after 40 charge–discharge cycles that is 50% of the initial value. This partial decay of the cell performances may be attributed to a still not optimized cell balance, and can be addressed by setting-up a proper positive-to-negative electrode ratio. Even preliminary, this result is encouraging, in particular if compared with the electrochemical response of a cell using the pristine TiO₂, without activation procedure, which is characterized by an almost complete capacity fading during the few initial cycles (data not reported). In our knowledge PEO-electrolyte solid cells using LiFePO₄ and TiO₂ electrode have

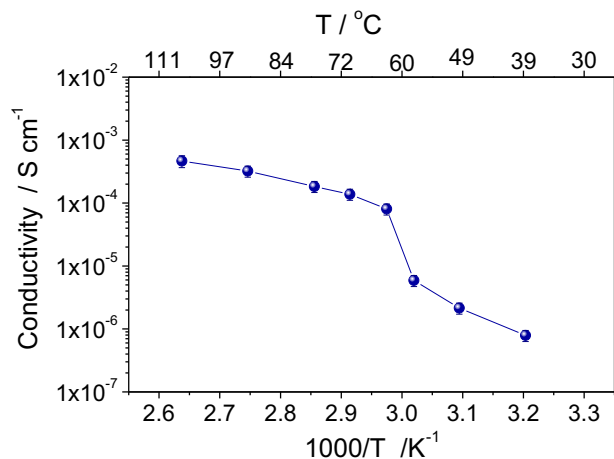


Fig. 3. Arrhenius plot of the PEO₂₀LiCF₃SO₃ + 10% w:w ZrO₂ electrolyte in the 40–110 °C temperature range.

never been reported, most likely due the issues above reported, associated with the TiO₂ surface irreversible reactions.

4. Conclusion

In this paper we reported the characterization of a solid polymer lithium ion cell using LiFePO₄ cathode, TiO₂ anode and PEO-based electrolyte. XRD, SEM and TEM characterization evidenced a pure TiO₂ phase with nanometric morphology, while electrochemical tests using conventional organic electrolyte of the two electrodes in half cells and of their combination in a full cell showed an enhanced electrochemical behaviour. Impedance spectroscopy characterization of the PEO-based electrolyte indicated good conductivity at temperatures higher than 60 °C and stable lithium–electrolyte interphase. The initial irreversible capacity of the TiO₂ has been reduced by the proper electrode treatment and the solid lithium ion cell evidenced an average working voltage of 1.8 V, a specific capacity of 150 mA h g^{−1}. However, a partial capacity fading associated with a still not fully optimized electrode–electrolyte interphase and cell balance has been observed. Therefore, additional investigation is required to address the cell balance and, in particular, to refine the direct activation procedure of the TiO₂ electrode. We believe that the optimization of these key aspects may lead to safe and environmentally friendly solid cells with enhanced characteristics in terms of cycle life and reversible capacity. Further work to reach this target is in progress in our laboratory, and the results will be reported in future papers.

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